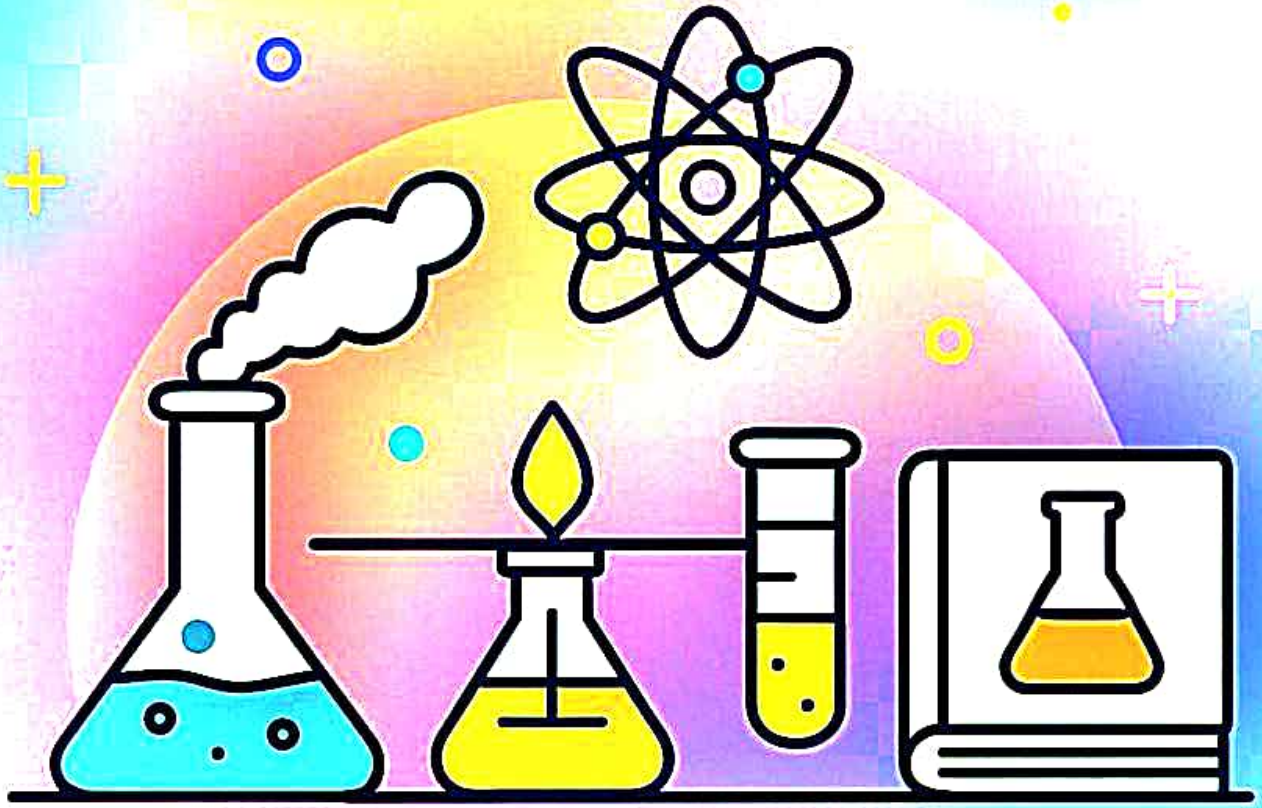
PHYSICAL CHEMISTRY

Formula Booklet



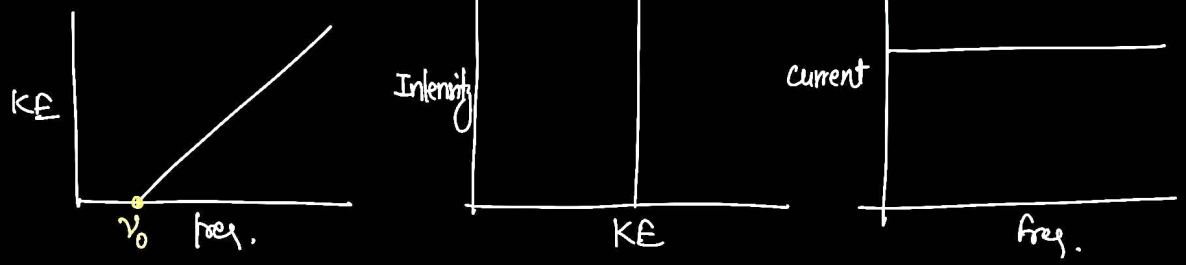
1. Atomic Structure

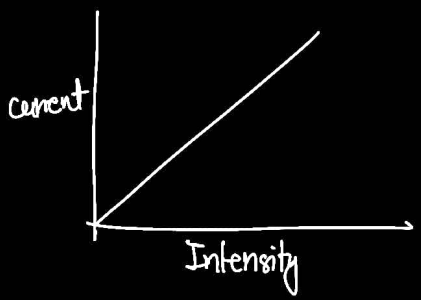
- distance of closest approach , $R = \frac{4KZe^2}{m_\alpha v_\alpha^2}$ — v_α: vel. of approaching α-particle

- Photoelectric effect

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$ ($\frac{1}{2}mv^2$: Max. KE)

$$\frac{1}{2}mv^2 = eV_s$$ (V_s: stopping potential)





- Quantum theory , $E = h\nu = \frac{hc}{\lambda}$ only for E.M. waves.

- De Broglie's Equation, $\lambda = \frac{h}{mv}$ — applicable for matter waves

- Bohr's model

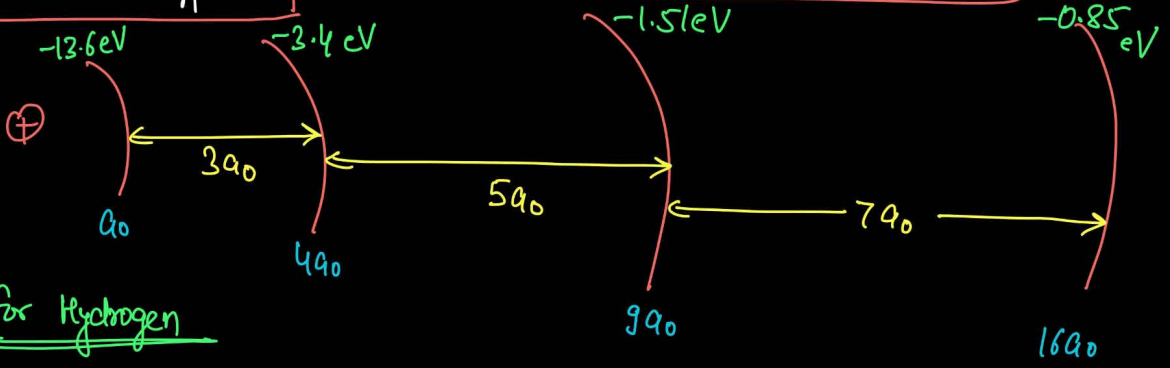
$mvr = \frac{nh}{2\pi}$ Quantisation of angular momentum

$E_n = -13.6\frac{Z^2}{n^2}$ eV/atom

$1\,eV = 1.6 \times 10^{-19}$ J

$r_n = \frac{n^2 a_0}{Z}$ $\quad a_0 = 0.529\ \text{Å}$ (Bohr's radius)

$v = 2.18 \times 10^6 \frac{Z}{n}\ ms^{-1}$ $\quad \therefore$ $r \propto \frac{n^2}{Z}$, vel. $\propto \frac{Z}{n}$



For Hydrogen

Freq. $= \frac{1}{\text{Time}}$ $\quad$ vel. $= \frac{\text{dist}}{\text{Time}} \Rightarrow$ time $= \frac{r}{v} = \frac{n^2/Z}{Z/n}$

Freq $\propto \frac{Z^2}{n^3}$ $\quad \therefore$ time $\propto \frac{n^3}{Z^2}$

* when a charged particle (q) is accelerated by V potential

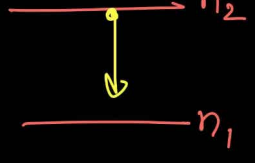
Gain in KE = work done

$\frac{1}{2}mv^2 = qV$

* For spectral lines

$\frac{1}{\lambda} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

n_1 : lower $\quad$ n_2 : higher



Lyman, $n \longrightarrow 1$ – UV

Balmer, $n \longrightarrow 2$ – visible

Paschen $n \longrightarrow 3$

Brackett $n \longrightarrow 4$ } IR

P-fund $n \longrightarrow 5$

$R = 109678\ cm^{-1}$ (Rydberg's const)

- $n \longrightarrow 1$ $\quad$ no. of spectral lines $= \frac{n(n-1)}{2}$

- $\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$ $\quad$ $\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$

- Quantum Numbers

  - Orbital angular momentum, $L = \sqrt{l(l+1)}\,\frac{h}{2\pi}$
  - spin moment , $\sqrt{n(n+2)}\,\frac{h}{2\pi}$
  - Max. orbitals in a subshell = $2l+1$
  - Max e^- ——— = $2(2l+1)$

Mole Concept

- specific gravity = $\frac{\text{density of substance}}{\text{density of water at } 4^\circ C}$

$V.D = \frac{\text{Mol. wt}}{2}$

- Mole = $\frac{\text{Given wt}}{\text{At or Mol. wt}} = \frac{\text{Given vol. of gas}}{\text{Molar vol. of gas}} = \frac{\text{No. of particles}}{N_A}$

- Molarity (M) = $\frac{\text{no. of moles of solute}}{\text{vol. of solution (Lt)}}$

- molality (m) = $\frac{\text{moles of solute}}{\text{wt of solvent (kg)}}$ → Temp. independent

- Mole fraction of solute = $\frac{\text{moles of solute}}{\text{Total moles}}$

- % by mass or w/w % = $\frac{\text{wt of solute (gm)}}{\text{wt of solution (gm)}} \times 100$

- % by vol. or V/V % = $\frac{\text{vol. of solute (ml)}}{\text{vol. of solution (ml)}} \times 100$

- PPm = $\frac{\text{solute particle}}{\text{Total part}} \times 10^6$
  = $\frac{\text{solute mass}}{\text{Total mass}} \times 10^6$
  = $\frac{\text{solute vol}}{\text{Total vol}} \times 10^6$

$$\% \ w/v = \frac{\text{wt of solute}}{\text{vol. of solution}} \times 100$$

* Molarity = moles of solute in 1000 ml | wt of 1000 ml = 1000d

$$m = \frac{M \times 1000}{1000d - MW}$$

* $$\text{Eq. wt} = \frac{\text{At or Mol. wt}}{\text{n-factor}}$$

n-factor for elements = valency
for salt = cationic or anionic charg
for acids = basicity (H^+ it can give per molecule)
for bases = acidity (H^+ ——— gain ———)

* Normality = n-factor × Molarity

No. of Eq = n-factor × no. of moles

* Dilution → amt. of solute is conserved

mole before dilution = mole after dilution

$$M_1V_1 = M_2V_2$$

* $$\% \text{ of any component} = \frac{\text{wt of component}}{\text{Mol. wt}} \times 100$$

* $$\text{Hardness of water in ppm} = \frac{\text{mass of } CaCO_3}{\text{Total mass of water}} \times 10^6$$

* **Vol. Strength of H_2O_2**

Normality of H_2O_2 (N) = $\frac{\text{Vol. Strength of } H_2O_2}{5.6}$

Molarity of H_2O_2 (M) = $\frac{\text{vol. strength of } H_2O_2}{11.2}$

Gaseous State

- $PV = nRT$

P = const → Charle's law, $V \propto T$

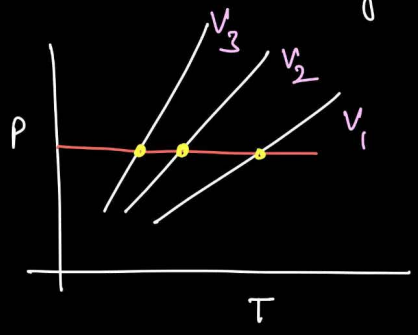
T = const → Boyle's law, $P \propto \frac{1}{V}$

same P, T → Avogadro's law, $V \propto n$

V = const → Gay Lussac's law, $P \propto T$

- $d = \frac{PM}{RT}$

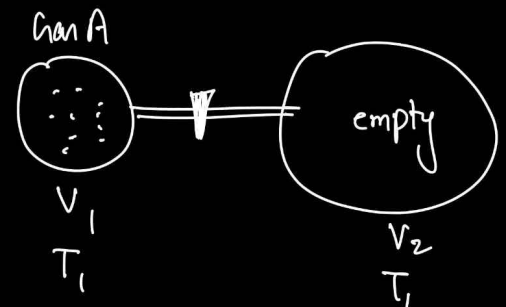
$V_1 > V_2 > V_3$



$PV = nRT$

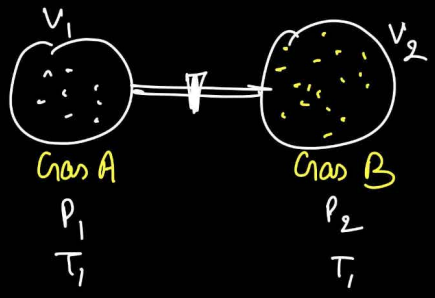
↓ const

$V \propto T$

- 

only vol. is ↑ and T = const

$\therefore P \propto \frac{1}{V}$ or $P_1V_1 = P_2V_2$

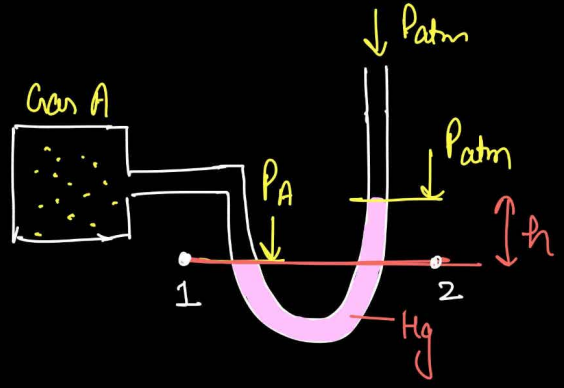


when valve is opened

moles of gas are conserved

$$\frac{P_1V_1}{RT_1} + \frac{P_2V_2}{RT_1} = \frac{P(V_1+V_2)}{RT_1}$$

•



$P_1 = P_2$

$P_A = P_{atm} + \rho g h$

• **Dalton's law :**

$PV = nRT$

A + B + C

$P_{Total} = P_A + P_B + P_C$

$\therefore P_A = P_{Total} \cdot X_A$

• **Graham's law**

Rate of effusion $\propto \frac{PA}{\sqrt{TM}}$

P → Press. of gas

A → area of cross-section of hole

M → Mol. wt of gas

T → Temp.

$Rate_A = \frac{\text{vol. of gas escaped}}{\text{Time taken}} = \frac{\text{mole escaped}}{\text{Time taken}} = \frac{\text{dist travelled}}{\text{Time taken}}$

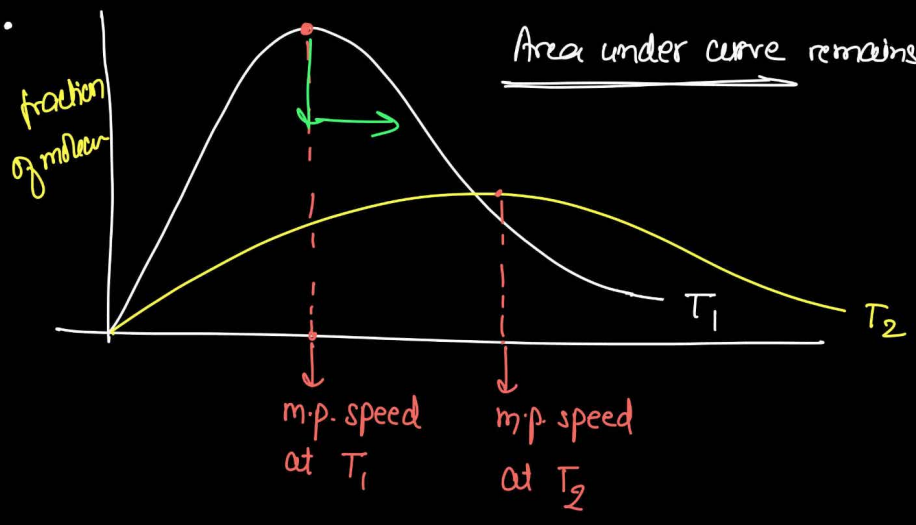
* **KTG**

$\frac{1}{2}mv^2 \propto$ abs. temp $\therefore$ $v^2 \propto T$, $v \propto \sqrt{T}$

• $U_{mp} : U_{arg} : U_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$

$1 : 1.128 : 1.224$

• Avg KE. per mole $= \frac{3}{2}RT$, Avg KE per particle $= \frac{3}{2}kT$



- $P_{id} \cdot V_{id} = nRT$

$$\left(P_{Real} + \frac{n^2a}{V^2}\right)\left(V_{Real} - nb\right) = nRT$$

$$= nRT$$

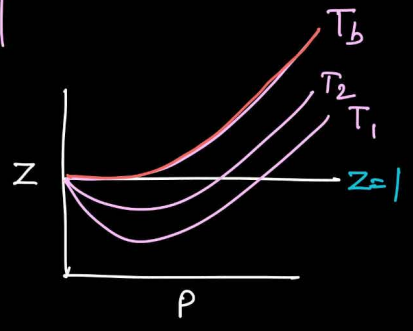
P_{id} V_{id}

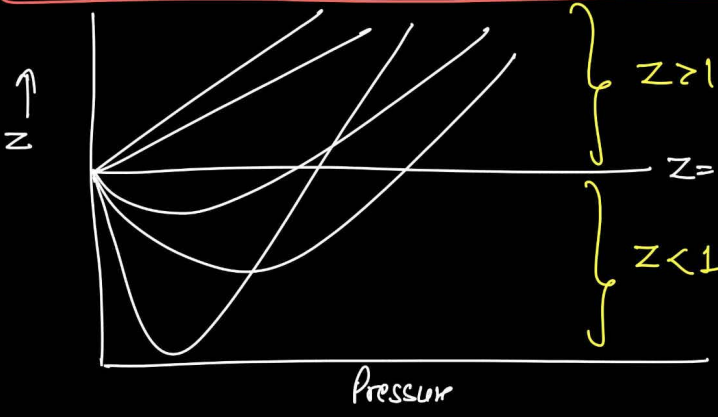
— Vander Waals Equation

- Z = compressibility factor = $\frac{V_{Real}}{V_{ideal}} = \frac{P_{id} \cdot V_{Real}}{RT}$

- $T_B = \frac{a}{Rb}$ = Boyle's Temp. , $T_i = \frac{2a}{Rb}$

$T_C = \frac{8a}{27Rb}$, $P_C = \frac{a}{27b^2}$, $V_C = 3b$





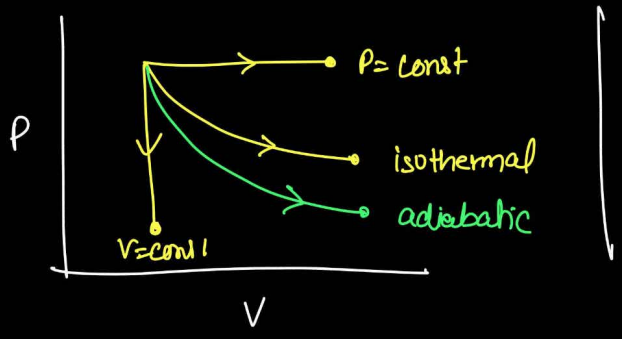
$Z > 1 \Rightarrow$ Repulsion dominant

$Z < 1 =$ attraction dominant

Thermodynamics

→ applications
→ limitations

- Isothermal Process, $T = \text{const}$, $dT = 0$, $\Delta T = 0$
- Isobaric " , $P = \text{const}$, $dP = 0$, $\Delta P = 0$
  Isochoric " , $V = \text{const}$, $dV = 0$, $\Delta V = 0$
  Adiabatic " , $q = 0$ (entropy is const in rev. adiabatic process)



Slope of adiabatic curve = γ × slope of isothermal curve

- FLOT :→ $dU = dq + dw$
  $\Delta U = nC_v\Delta T$ → Not applicable for phase change
  $\Delta H = nC_p\Delta T$

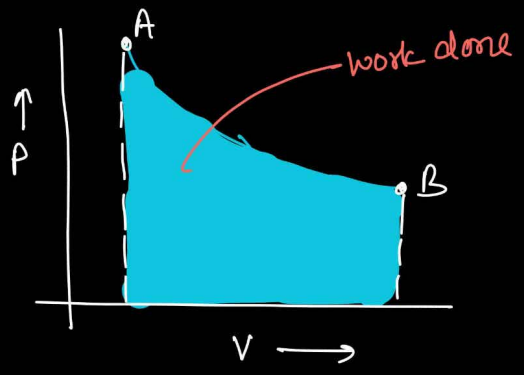
; $C_p - C_v = R$

; $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0$

I.E. of ideal gas depends only on temp.

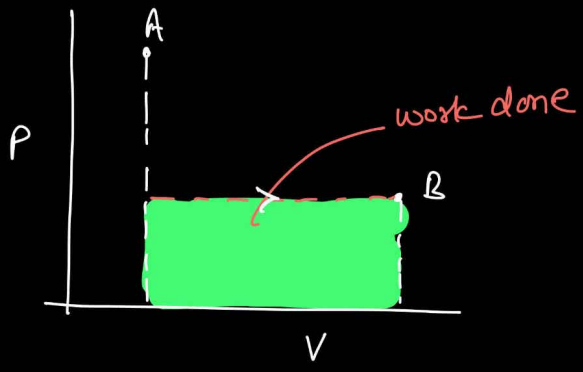
- $W_{\text{Rev iso}} = -2.303nRT \log \frac{V_2}{V_1} = -2.303\, nRT \log \frac{P_1}{P_2}$

$W_{\text{IRR. iso}} = -P\Delta V$



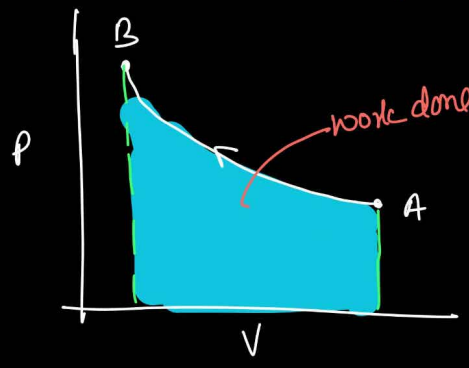
Rev. isothermal expansion

W_{exp} = -ve

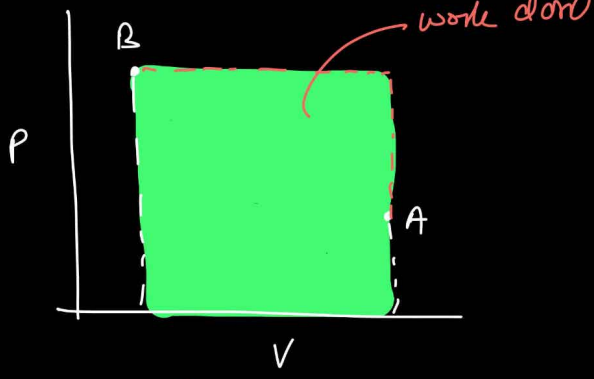


IRR. Iso. Expansion

$|W_{Rev\ exp.}| > |W_{IRR\ exp.}|$



Rev. iso compression



IRR. iso compression

$W_{IRR.\ comp} > W_{Rev.\ comp.}$

- W (isochoric) $= -P_{ext} \Delta V = 0$ ($\Delta V \to 0$)
  W (Isobaric) $= -P_{ext} \Delta V$

- **Adiabatic Process**

(a) Rev. adiabatic

$PV^{\gamma} = const$

$TV^{\gamma-1} = const$

$T^{\gamma} P^{1-\gamma} = const$

(b) IRR. adiabatic

- $W = \Delta U = nC_v \Delta T$

$= \frac{nR(T_2 - T_1)}{\gamma - 1}$

$= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

- $W = \Delta U = nC_v\Delta T$

$= \frac{nR(T_2 - T_1)}{\gamma - 1}$

$= \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

* T_{final} (Rev. adia) < T_{final} (IRR. adia)

* **Enthalpy** ⟹ heat exchange at const pressure

$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P$

$= \Delta U + \Delta n_g RT$

$= \Delta U + nR\Delta T$

$= nC_p\Delta T$

ΔU = heat exchange at const volume

* $dS = \frac{dq_{rev}}{T}$; $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{B.P.}}$, $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_{F.P.}}$

$\Delta S_{sys} = nC_v \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$

- For Isothermal : $\Delta S = nR \ln\frac{V_2}{V_1}$ or $nR \ln\frac{P_1}{P_2}$
- Adiabatic ; $\Delta S_{sys} = 0$; $\Delta S_{surr} = 0$ (Rev. adiabatic)

  $\Delta S_{sys} = 0$; $\Delta S_{surr} > 0$ (IRR. adiabatic)
- Isobaric : $\Delta S = nC_p \ln\frac{V_2}{V_1}$
- Isochoric : $\Delta S = nC_v \ln\left(\frac{P_2}{P_1}\right)$

* $G \equiv U + PV - TS = H - TS$

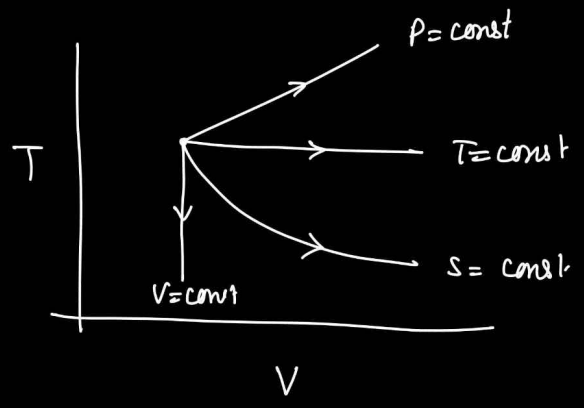
$\Delta G = \Delta G - T\Delta S - S\Delta T$

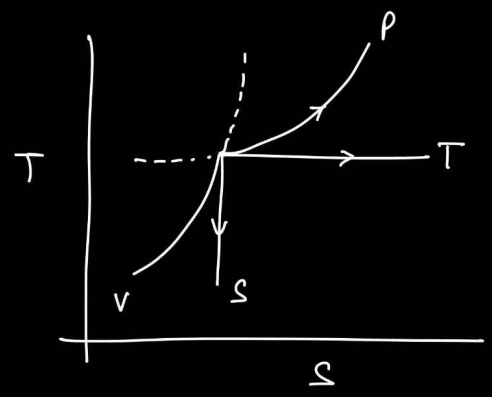
$dG = VdP - SdT$ for a closed system

→ $T = const$, $dG = VdP \Rightarrow V = \left(\frac{dG}{dP}\right)_T$

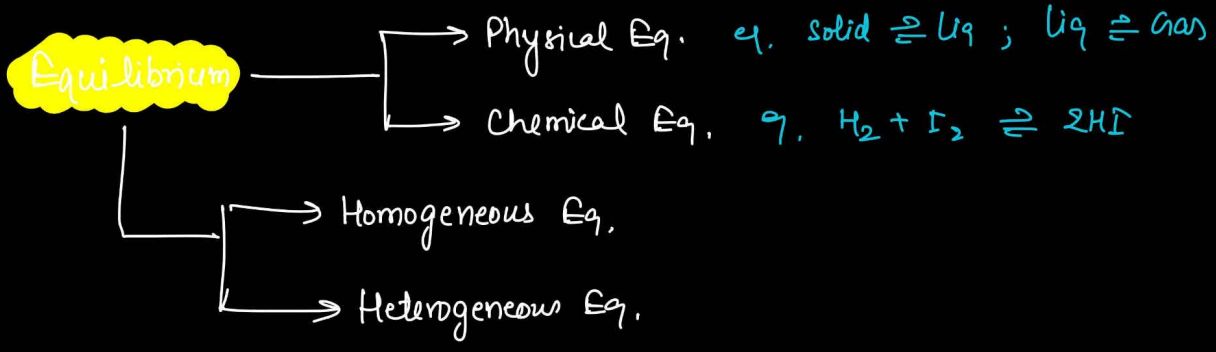
→ $P = const$, $dG = -SdT \Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P$

- $\Delta G_{sys} = -T\Delta S_{univ.}$
- $\Delta G = \Delta G^{\circ} + 2.303RT \log Q$





Chemical Equilibrium



- $aA + bB \rightleftharpoons cC + dD$

  at Eq. $R_f = R_b$ and $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ $Q = K_{eq}$ at Eq.

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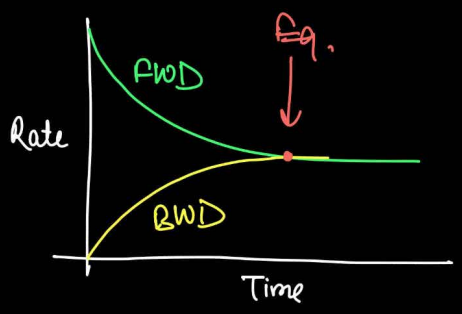
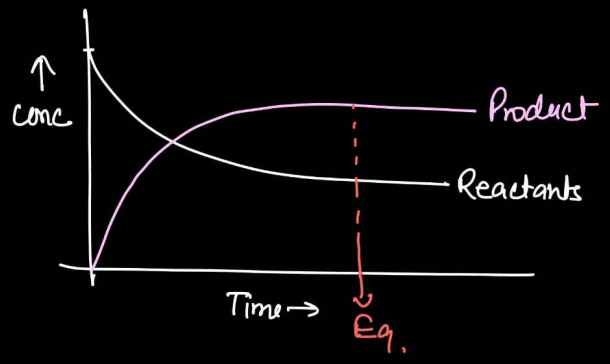




- $\Delta G = \Delta G^\circ + 2.303\,RT \log Q$

  zero at Eq — K_{eq}

  $\therefore \quad \Delta G^\circ = -2.303\,RT \log K_{eq}$

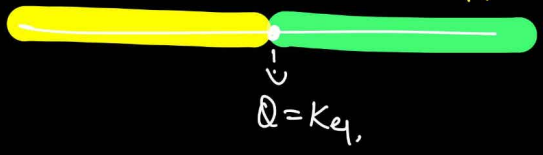
- $K_p = K_c(RT)^{\Delta ng}$

  $K_p = K_x \cdot P^{\Delta ng}$

  P → Total Pressure

Rxn goes FWD: $Q < K_{eq}$.

Rxn goes BWD: $Q > K_{eq}$.

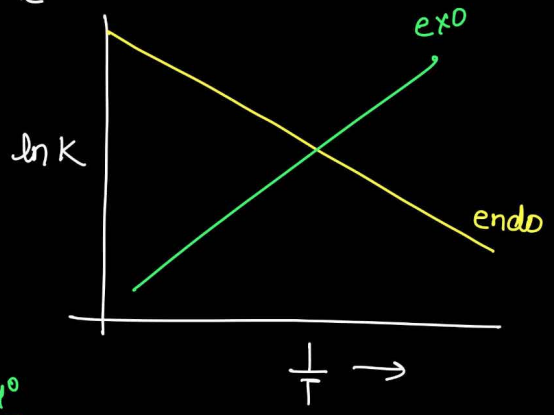


- Magnitude of K_{eq}
  - High $(> 10^3)$ ⇒ [Product] >> [Reactant]
  - low $(< 10^{-3})$ ⇒ [Reactant] >> [Product]

- $K_{eq.}$ → doesn't depend on conc. of reactants, products.
  presence or absence of catalyst
  pressure
  volume

  depends on temp. only

- $$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



$$\ln K = \frac{-\Delta H^\circ}{RT} + \text{const}$$

$$y = mx + c$$

$$\text{slope} = -\frac{\Delta H^\circ}{R}$$

When ΔH = +ve; -ve slope
ΔH = -ve; +ve slope

- $$\frac{D}{d} = 1 + (n-1)\alpha$$

  D = V.D. before dissociation
  d = V.D. after dissociation

$A_n(g) \rightleftharpoons nA(g)$

Ionic Equilibrium

- **Ostwald dilution law** (only for weak electrolytes)

$HA \rightleftharpoons H^+ + A^-$; $K_a = \frac{[H^+][A^-]}{[HA]}$

$\alpha = \sqrt{\frac{K_a}{C}}$ (only if $\alpha < 0.1$)

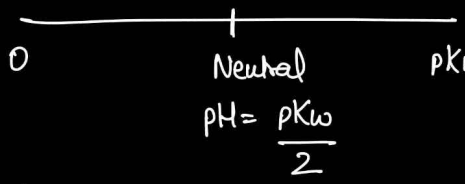
- $pH = -\log [H^+]$ ⟶

10^{-3} M HCl soln pH = 3

10^{-5} M HCl soln pH = 5

10^{-7} M HCl soln pH = 6.8

10^{-8} M HCl soln pH = 6.9



if $K_w = 10^{-14}$, $pK_w = 14$ ⇒ Neutral point = 7

$K_w = 10^{-12}$, $pK_w = 12$ ⇒ " " = 6

- **Absolute dissociation const of water**

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

$K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$ at 298 K

K_w = ionic product of water = $[H^+][OH^-] = 10^{-14}$ at 298 K

$K_a \cdot K_b = K_w$ $\quad$ $pK_a + pK_b = pK_w = 14$ at 298 K

- **pH calculation**

↳ Mix. of 2 strong acids = $\frac{\text{Total mole } H^+}{\text{volume}} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$ = conc. of H^+

2 strong bases = $\frac{\text{Total mole } OH^-}{\text{volume}} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$ = conc. of OH^-

↳ Mix. of an acid + base (strong)

if Eq. of acid (N_1V_1) > Eq. of base (N_2V_2) ⇒ $\frac{N_1V_1 - N_2V_2}{V_1+V_2} = [H^+]$

Eq. of base (N_2V_2) > Eq. of acid (N_1V_1)

↳ $\frac{N_2V_2 - N_1V_1}{V_1+V_2} = [OH^-]$

↳ pH of a weak monoprotic acid (HA)

$HA \rightleftharpoons H^+ + A^-$; K_a , $\alpha = \sqrt{\frac{K_a}{C}}$

$[H^+] = C\alpha = \sqrt{K_a \cdot C}$ ⇒ $pH = \frac{1}{2}(pK_a - \log C)$

↳ pH of a soln. of polyprotic acid (H_2A)

$pH = \frac{1}{2}(pK_{a_1} - \log C)$

- Salt Hydrolysis ⇒ ions of strong species don't undergo hydrolysis

Salt of	Type of Hyd.	K_h	h	pH
WA + SB	anionic hyd.	$\frac{K_w}{K_a}$	$\sqrt{\frac{K_w}{K_a \cdot C}}$	$7 + \frac{pK_a}{2} + \frac{\log C}{2}$
SA + WB	cationic hyd.	K_w/K_b	$\sqrt{\frac{K_w}{K_b \cdot C}}$	$7 - \frac{pK_b}{2} - \frac{\log C}{2}$
WA + WB	both	$\frac{K_w}{K_a \cdot K_b}$	$\sqrt{\frac{K_w}{K_a \cdot K_b}}$	$7 + \frac{pK_a}{2} - \frac{pK_b}{2}$
SA + SB	don't undergo hydrolysis			pH = 7

- **Buffer solution** → Resists change in pH
  - Acidic buffer — WA + salt with SB
  - Basic buffer — WB + salt with SA

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

$$pOH = pK_b + \log \frac{[salt]}{[Base]}$$

- **Indicators** →

$$HIn \rightleftharpoons H^+ + In^-$$

$$pH = pK_{HIn} + \log \frac{[In^-]}{[HIn]}$$

- **Titration with HCl**

	Phenolphthalein	Methyl Orange
NaOH (SB)	100% Rxn is indicated $NaOH + HCl \rightarrow NaCl + H_2O$	100% Rxn is indicated $NaOH + HCl \rightarrow NaCl + H_2O$
Na_2CO_3 (WB)	50% rxn upto $NaHCO_3$ stage is indicated $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	100% rxn is indicated $Na_2CO_3 + 2HCl \rightarrow H_2CO_3 + 2NaCl$
$NaHCO_3$	No Rxn indicated	100% rxn is indicated

- **Isoelectric Point** ⇒

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$$

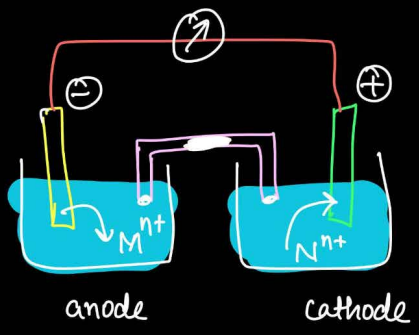
Electrochemistry

- anode half || cathode half

$E_{cell} = E_{RHS} - E_{LHS}$ $= +ve \Rightarrow$ cell is spontaneous

$= -ve \Rightarrow$ " " non-spontaneous

$= 0 \Rightarrow$ Equilibrium



- SRP value $\propto$ Ox. Power

  SOP value $\propto$ Red. Power

- $\Delta G = -nFE_{cell}$

  $\Delta G = \Delta G^\circ + 2.303\,RT \log Q$

  $-nFE = -nFE^\circ + 2.303\,RT \log Q$

$$E = E^\circ - \frac{2.303\,RT}{nF} \log Q$$

→ ensure you have balanced the given cell equation.

→ no. of e^- participating in balanced eqn.

$M^{2+} + X \longrightarrow X^{2+} + M$

$$Q = \frac{[X^{2+}]}{[M^{2+}]}$$

At Eq. $E_{cell} = 0$, $\Delta G = 0$

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_{eq.}$$

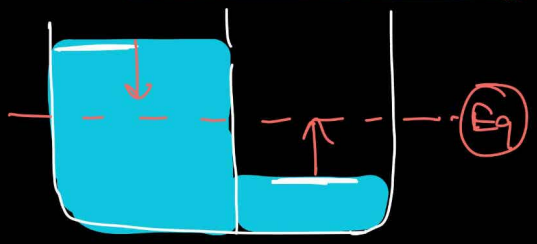
- **Concentration cell** : same cells but diff conc.

eg. $Zn(s) \mid Zn^{2+}(C_1) \parallel Zn^{2+}(C_2) \mid Zn(s)$

$E = \cancel{E^0}^{0} - \frac{0.0591}{2} \log \frac{C_1}{C_2}$

$E = \frac{0.0591}{2} \log \left(\frac{C_2}{C_1}\right)$

$E_{cell} > 0$ if $C_2 > C_1$



- Metal–Metal insoluble salt electrode

$$E_{Cl^-|AgCl|Ag} = E^\circ_{Cl^-|AgCl|Ag} - 0.0591 \log [Cl^-]$$

- $dG = \cancel{VdP}^{0} - SdT$

at const P, $dG = -SdT \Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_P$

$$\Delta S = -\left[\frac{d(\Delta G)}{dT}\right]_P = \left[nF\left(\frac{dE_{cell}}{dt}\right)\right]_P$$

→ temp. coefficient

- **Electrolysis** → Non-spontaneous
  - higher SRP ⟶ deposited first

$K^+, Ca^{2+}, Na^+, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}$

Increasing order of deposition

increasing SRP

- **Faraday's laws**
  - 1 Faraday deposits 1 Equivalent

$$w = zit = \frac{Eit}{96500}$$

E = Eq. wt
i = current in Amp.
t = time in sec

- When cells are connected in series, same amt. of charge flows through them
  ⇓
  Eq. deposited are same in all connected cells.

- Conductance $= \frac{1}{\text{Resistance}}$

$R = \rho \frac{l}{A}$, $\frac{1}{\rho} = \frac{l}{A} \cdot \frac{1}{R}$

K = cell const. $\frac{1}{R}$

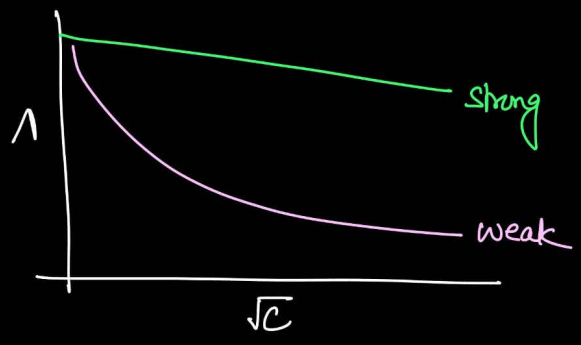
K = sp. conductance
$K \downarrow$ on dilution
↓
$S\,cm^{-1}$ or $S\,m^{-1}$

- $\Lambda_m = \frac{K \times 1000}{\text{Molarity}}$; $\Lambda_{eq} = \frac{K \times 1000}{\text{Normality}}$

- Kohlrausch's law

$$\Lambda_m = \Lambda_M^\infty - b\sqrt{C}$$

$\Lambda_m \uparrow$ on dilution



- For an electrolyte

$$\Lambda_\infty = n_+ \lambda_+^\infty + n_- \lambda_-^\infty$$

eg. $K_2SO_4 \Rightarrow \Lambda_m^\infty = 2\lambda_m^\circ(K^+) + \lambda_m^\circ(SO_4^{2-})$ (Molar conductance)

$\Lambda_{eq}^\infty = \lambda_{eq}^\circ(K^+) + \lambda_{eq}^\circ(SO_4^{2-})$

- $\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$

Solutions & Colligative Properties

Homogeneous mix.

Solubility → Nature of solute & solvent
→ Temp.
→ Pressure (for gaseous solute)

Solubility ↑ with T ↑ if ΔH = +ve
↓ with T ↑ if ΔH = -ve

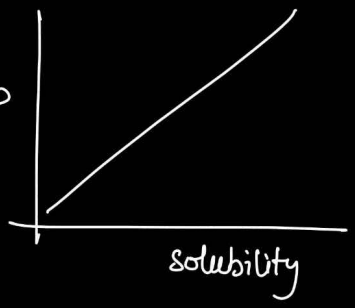
- **Henry's law** $p \propto x$

$p = K_H x$ (gas)

$x = K'_H p$

$K_H \propto \frac{1}{\text{solubility}}$

$\text{solubility} \propto \frac{1}{\text{Temp.}}$



Gases

- V.P. is independent of → amt. of substance
→ surface area
→ shape of vessel

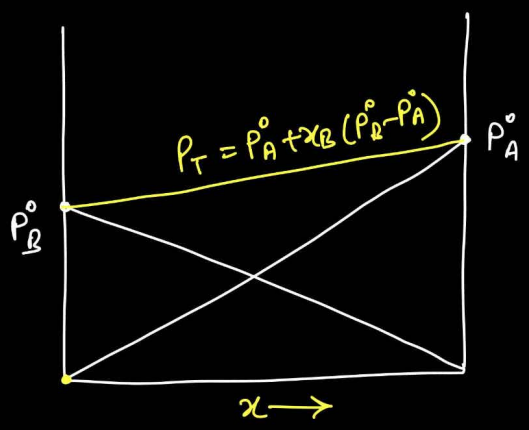
V.P. depends on Temp. only

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

- **Raoult's law** V.P. of solution

$P_A = P_A^\circ x_A$, $P_B = P_B^\circ x_B$

$P_{Total} = P_A + P_B = P_A^\circ + x_B(P_B^\circ - P_A^\circ)$



Solution → obey Raoult's law → ideal solutions

→ Do not obey → Non-ideal → +ve deviation
−ve deviation

Ideal Soln

$\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$

$\Delta G_{mix} = -ve$, $\Delta S_{mix} = +ve$

A—A, A—B, B—B } equivalent attraction

+ve deviation ⇒ weaker attractive forces

- $\Delta H_{mix} = +ve$
- $\Delta V_{mix} = +ve$
- $\Delta S_{mix} = +ve$
- $\Delta G_{mix} = -ve$

eg. $H_2O + CH_3OH$ or C_2H_5OH

C_2H_5OH + Hexane

$CHCl_3 + CCl_4$

−ve deviation ⇒ stronger attractive forces

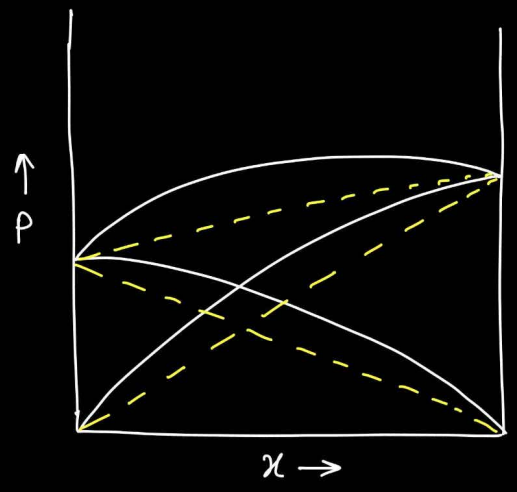
- $\Delta H_{mix} = -ve$
- $\Delta V_{mix} = -ve$
- $\Delta S_{mix} = +ve$
- $\Delta G_{mix} = -ve$

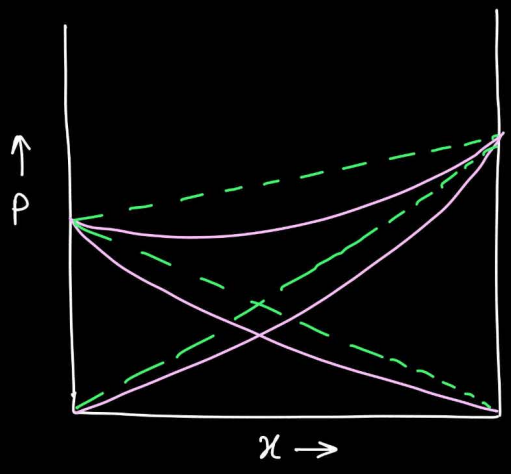
eg. $H_2O + HCOOH$

$H_2O + CH_3COOH$

$H_2O + HNO_3$

$CHCl_3$ + acetone





- Colligative Prop. → depend only on no. of particles
  - → RLVP
  - → ΔT_b
  - → ΔT_f
  - → π

RLVP

- $\frac{P^\circ - P_s}{P^\circ} = i X_{solute}$

P° = Press. of solvent
P_s = V.P. of solution

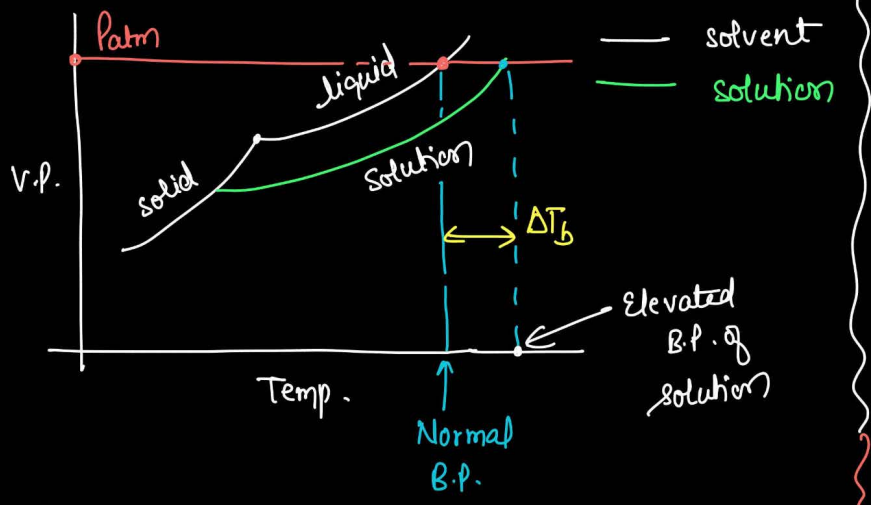
Rearrange to get

- $\frac{P^\circ - P_s}{P_s} = i \frac{n_{solute}}{n_{solvent}}$

ΔT_b

$\Delta T_b = i K_b \cdot m$ (m = molality; K_b of solvent)

$K_b = \frac{R T_b^2 M_{solvent}}{1000 \Delta H_{vap}}$



$\Pi = i CRT$

$i = \frac{\text{exp./observed/actual value of C.P.}}{\text{theoretical value of C.P.}} = \frac{\text{theoretical mass}}{\text{Exp. molar mass}}$

$i > 1$ for dissociation

$i < 1$ for association

$i = 1 + (n-1)\alpha$

n = no. of particles generated by 1 particle.

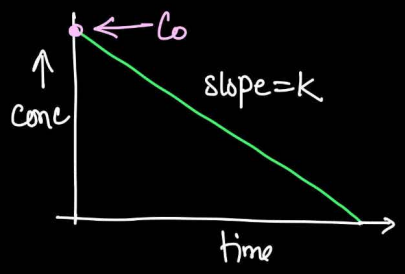
Chemical Kinetics

1. Zero order Rxn

$C_t = C_0 - kt$ linear drop

$t_{1/2} = \frac{C_0}{2K}$

$t_{100} = \frac{C_0}{K}$



- Equal amt. drops in equal time intervals.

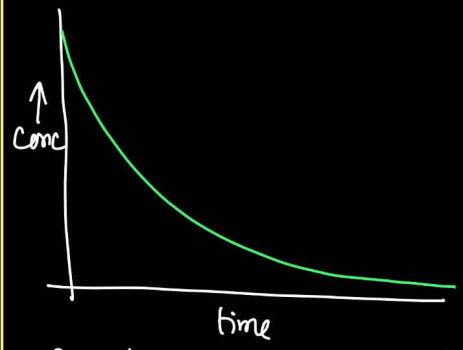
$100 \xrightarrow{t} 80 \xrightarrow{t} 60 \xrightarrow{t} 40 \xrightarrow{t} 20 \xrightarrow{t} 0$

2. First Order Reaction

$C_t = C_0 e^{-kt}$ $\quad \ln\left(\frac{C_0}{C_t}\right) = kt$

$k = \frac{2.303}{t} \log \frac{C_0}{C_t}$ $\quad t_{1/2} = \frac{0.693}{K}$

$t_{75\%} = 2 \times t_{1/2}$



- Equal % drops in equal time intervals

$100 \xrightarrow[50\%.]{t} 50 \xrightarrow{t} 25 \xrightarrow{t} 12.5 \xrightarrow{t} 6.25 \ldots$

$100 \xrightarrow[20\% \downarrow]{5\,min} 80 \xrightarrow[20\% \downarrow]{5\,min} 64$

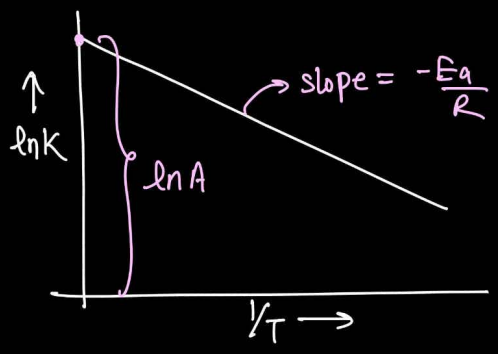
- $t_{1/2} \propto (\text{Conc.})^{1-n}$
- Arrhenius Equation

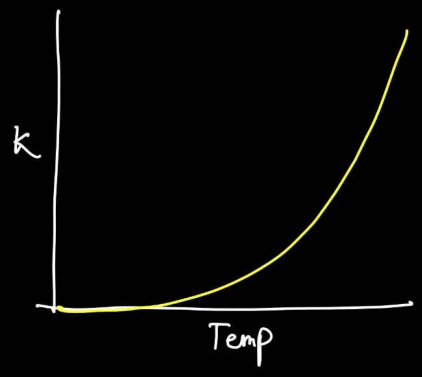
$k = Ae^{-E_a/RT}$

$\ln K = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A$

$y = mx + c$

as $T \uparrow$, $k \uparrow$ $\therefore$ Rate of Rxn $\uparrow$





$$\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Solid State

	a	Packing eff.	Z	C.N.
• Simple Cubic	$a = 2r$	52%	1	6 at dist. a
• BCC	$\sqrt{3}a = 4r$	68%.	2	8 at $\sqrt{3}a/2$
• FCC	$\sqrt{2}a = 4r$	74%.	4	12 at $a/\sqrt{2}$

- density of unit cell = $\frac{\text{Mass of unit cell}}{\text{vol. of unit cell}} = \frac{Z\,M}{N_A} \cdot \frac{1}{a^3}$

  $\frac{Z\,M}{N_A}$ → Mass of unit cell; $\frac{1}{a^3}$ → vol. of unit cell

-

C.N.	LRR (r^+/r^-)
3	0.155 – 0.225 (triangular)
4	0.225 – 0.414 (Tetrahedral)
6	0.414 – 0.732 (Octahedral)
8	0.732 – 0.999 (Cubic)

- Size of voids: Cubic > Octahedral > tetrahedral > trigonal

- Rock Salt Structure (NaCl) → Na^+ = at every OHV
  Cl^- = at lattice sites (FCC)
  C.N. = 6:6
  4 formula units/unit cell
  $a = 2(r^+ + r^-)$

- CsCl Structure → CN: 8:8 → Cs^+ = cubic void
  → Cl^- = Cubic corners.
  1 formula unit/unit cell , $\sqrt{3}a = 2(r^+ + r^-)$

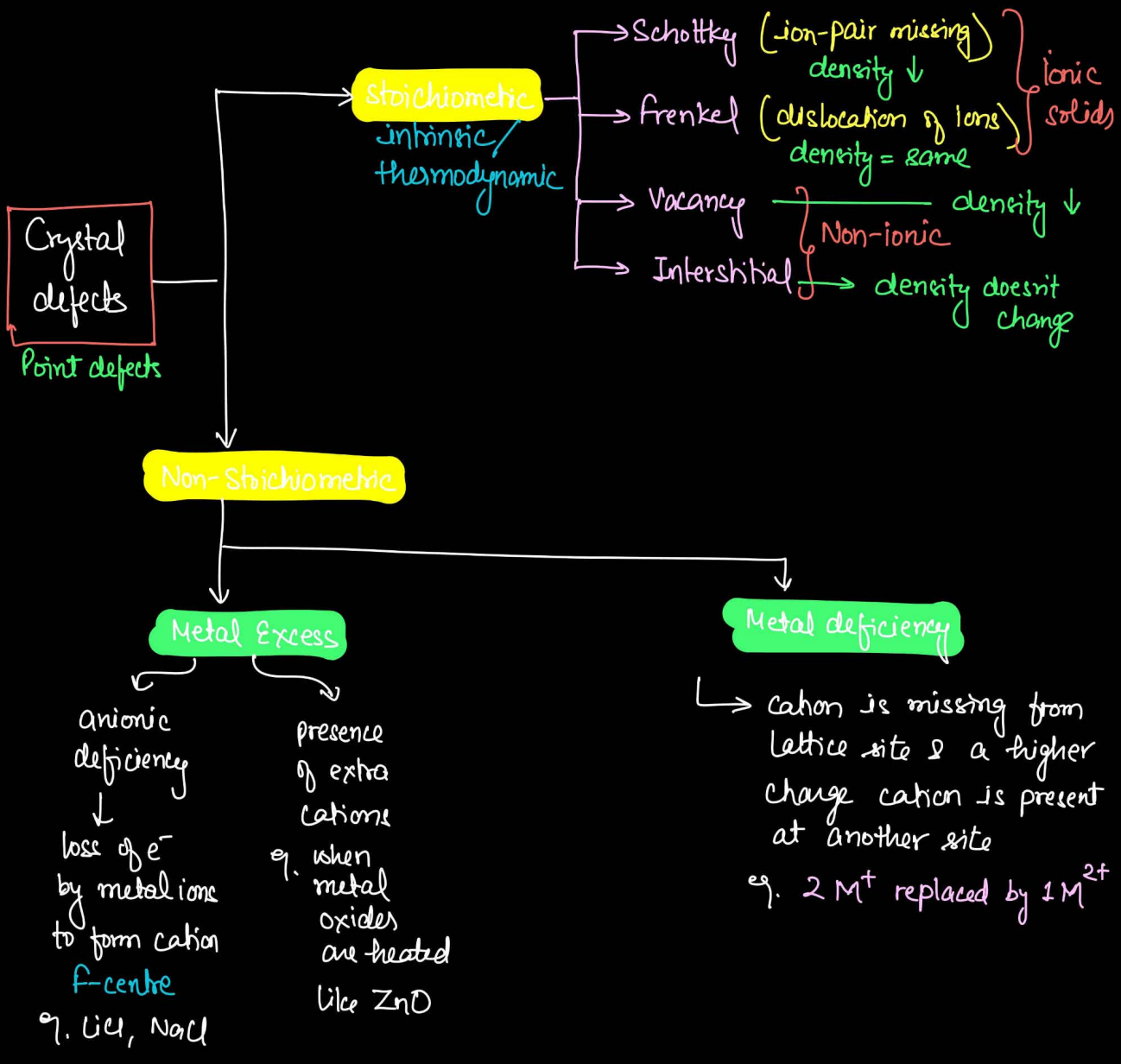
- ZnS Structure → CN: 4:4
  - → Zinc Blende (Most common) → CCP
  - → Wurtzite (Rare) → HCP

Zinc Blende

CCP → Zn^{2+} : 50% of THV (alternate THV)
→ S^{2-} : at CCP sites

$r^+ + r^- = \frac{1}{4} \cdot \sqrt{3}\, a$

* Diamond structure → like ZnS
  → every location is occupied by C.
  $Z = 8$


Crystal defects
Point defects
Stoichiometric
intrinsic / thermodynamic
Schottky (ion-pair missing) density ↓
Frenkel (dislocation of ions) density = same
Ionic solids
Vacancy
Interstitial
Non-ionic
density ↓
density doesn't change
Non-Stoichiometric
Metal Excess
anionic deficiency
↓
loss of e⁻ by metal ions to form cation
F-centre
eg. LiCl, NaCl
presence of extra cations
eg. when metal oxides are heated like ZnO
Metal deficiency
cation is missing from lattice site & a higher charge cation is present at another site
eg. 2 M⁺ replaced by 1 M²⁺